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THE STRENGTH OF IONIC SOLIDS

Tenth Technical Report

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INTRODUCTION

The mechanical behavior of ionic solids, particularly those of the rock-salt structure, has always been of great interest because of the straightforward and elegant experimental methods which have proved possible in the study of their plasticity and fracture characteristics. The processes of slip and twinning and the phenomenon of cleavage were in fact originally discovered in ionic solids and were studied intensively in the 1920's. The optical isotropy and transparency of certain of these crystals to wave lengths from infrared to ultraviolet has enabled stress birefringent effects to be used to examine, for example, internal distributions of slip and other sources of long range stress. Absorption spectra over the same range of wave lengths and electrical conductivity measurements have yielded direct information regarding the nature and mobility of point defects. More recently etch pit techniques have allowed detailed studies of individual dislocations, their generation and movement.

Three general areas of interest have gradually evolved, each of which were originally stimulated by the experimental convenience of ionic solids. In one, the principal theme is concerned with the nature of various types of point defects and the ways in which such defects can interact with each other and with dislocations. Of special importance are those effects which accompany the introduction of mono- and bi-valent cations into solid solution. For example, when Ca^{++} ions are added to sodium chloride crystals in mole fractions of the order 10^{-5}, they increase the flow stress by an amount 100 times that associated with an equivalent quantity of mono-valent cations even though they are of comparable ionic size.[1] Recent authors have considered the role played by the cation vacancies which must accompany the introduction of bi-valent cations to rock salt in order to maintain electrical neutrality.[2,3] Particular attention has been given to the electrostatic interactions between point defects and dislocations. Pratt has reviewed these aspects of the strengthening of ionic solids in detail.[4]

The direct observation of individual dislocations was first made in ionic crystals and represents another important area of interest. [5] For example, Mitchell and his co-workers and Amelinckx have analysed the geometrical configurations of static dislocation distributions in silver halides and alkali halides respectively. [6][7] The elegant experimental observations of Gilman and Johnston, who employed etch pit techniques, have led to a better understanding of how slip bands grow through the cross-slip and multiplication of screw dislocations. [8][9] They have measured the effect of shear stress and temperature upon the velocity of dislocations and have related these observations to macroscopic plastic behavior. [10] Recently electron transmission techniques have been successfully applied to the study of dislocations in thin films of ionic solids. [11]

The third area of interest stems from the intensive studies made in Europe in the 1920's already reviewed in detail in the classic book by Schmid and Boas. [12] One of the more intriguing observations of this period was made by Joffe, et al, who demonstrated that embrittled rock salt became ductile whem immersed in water, an observation which was to spawn many experiments designed to understand the effect of environment upon ductility. [13] More recently, the demonstration by Parker and his co-workers that magnesium oxide crystals could be bent plastically at room temperature, and the work of Wachtman and Maxwell and Kronberg on the plastic behavior of alumina crystals at elevated temperatures focused attention on the fundamental behavior of refractory ionic solids. [14][15][16]

While ionic solids still provide the means of making significant contributions to our knowledge of the mechanical behavior of solids in general, there is now an additional motive, the need for a critical evaluation of the factors which limit the strength of ceramic materials in both mono and polycrystalline forms.

In this paper we shall regard the strengthening of ionic solids in terms of the microstructural factors affecting their resistance to cleavage fracture, for it

is a characteristic feature of these semi-brittle solids that their mechanical properties are to a great extent dominated by the nucleation and growth of cleavage cracks. We shall confine our attention to four solids which have the rock salt structure, namely, magnesium oxide, sodium chloride, lithium fluoride and silver chloride. These are selected not only because they have been the most extensively investigated, but also because the mechanical behavior of these solids have many features in common which enable useful generalities to be drawn.

One of the most stimulating of these generalities concerns the relation of silver chloride to the other three solids. It has long been thought that, in terms of mechanical behavior, silver chloride is a unique material in view of its extreme ductility at room temperature. However, it has recently been demonstrated that at a sufficiently low temperature it too becomes brittle at high strain rates and fractures by cleavage. [17] The special feature of silver chloride which distinguishes it from the other solids is that it manifests the same fracture phenomena at a much lower temperature relative to its melting point under the same loading conditions. One example of this relationship concerns the ductile to brittle transition temperature as measured on polished single crystals. Curves of the energy absorbed under impact bending (10 inch lb. energy input, strain rate 100 sec^{-1}) for the four respective solids are reproduced in Figure 1, from which it may be seen that silver chloride undergoes a transition at 0.2 Tm (-196°C) while the others do so at 0.6 - 0.7 Tm. The usefulness of this relationship, once established, is that it enables one to anticipate how the other solids will behave by performing exploratory experiments on silver chloride in a more convenient temperature range. The degree to which the relationship holds will be qualified in later sections.

In the next section we will describe experiments which emphasize the notch sensitivity of ionic solids, in the third section a number of ways in which notches are known to be formed will be presented and finally we will discuss the conditions under which such notches propagate for brittle fracture.
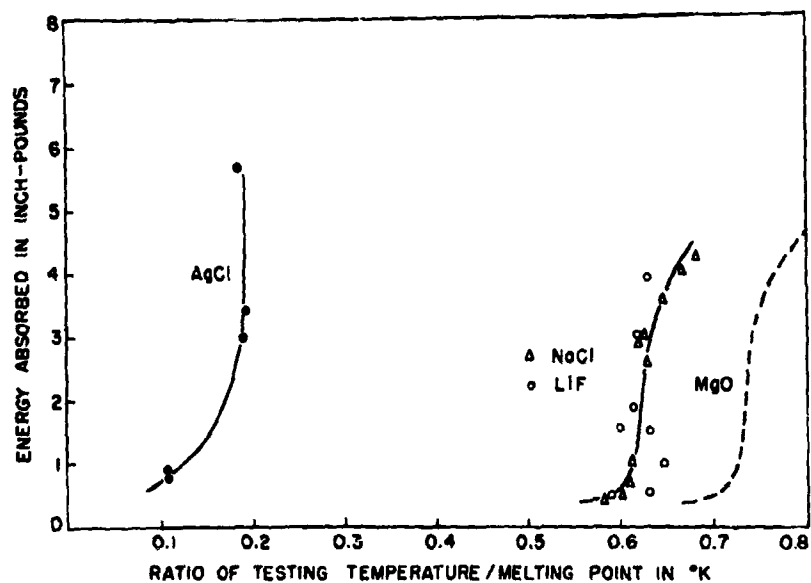
Figure 1 - Ductile-brittle transition curves for polished mono-
crystals of silver chloride (cubic orientation), sodium
chloride, lithium fluoride and magnesium oxide impacted
at a nominal maximum strain rate of 100 sec^{-1}

NOTCH SENSITIVITY OF IONIC SOLIDS

One of the most important consequences of the tendency of ionic solids to
cleave is their notch sensitivity, particularly when the notch is present as
a small cleavage crack. While notch sensitivity is shared by many semi-
brittle solids, the distinguishing feature of ionic solids is the degree to which
they are notch sensitive. This is manifested in a number of ways, two of
which will now be described while others will become apparent during the
course of the paper.

First, there is the consequence of surface damage in the form of minute
cleavage cracks on the low strain rate (10^{-5} sec^{-1}) tensile properties of
single crystals at room temperature.[18] The defects may be introduced
accidentally in the course of handling such crystals or deliberately by im-
pacting them with fine hard particles (eg, 200 mesh silicon carbide powder).
It has been shown that damage of this kind limits the ductility of sodium
chloride monocrystals to only 2-5% elongation. When special precautions
are taken to prepare flaw-free surfaces, similar crystals can be elongated
in tension by as much as 50%, a ten-fold improvement. A composite photo-
micrograph illustrating the elongation which can be achieved with carefully
treated crystals is included in Figure 2. However, even these 'ductile'
sodium chloride crystals fracture catastrophically be cleavage from an in-
ternal flaw generated during the course of plastic flow, as shown in Figure
3. While in the complete absence of a clevage notch these single crystals
may be extremely ductile, they are nevertheless, still notch sensitive for
as soon as a notch is formed either internally or externally, catastrophic
fracture by cleavage quickly foliows. Surface condition is similarly impor-
tant in the mechanical behavior of lithium flouride and magnesium oxide
under these conditions.[18]
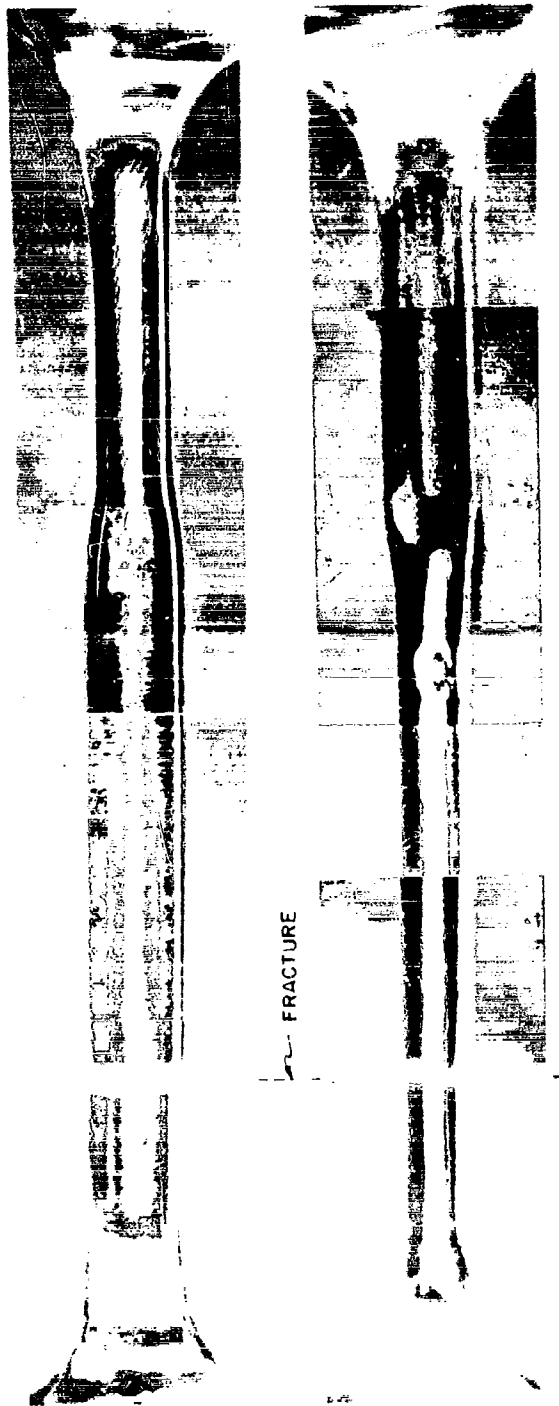
FRACTURE

Figure 2 – Two orthogonal views of a sodium chloride crystal elongated 50% in tension. Crystal had a carefully pre-pared polished surface. Note that each half of the crystal has slipped on two (110) planes having a common zone axis (x 10).

Figure 3 - Fracture surface of the sodium chloride crystal in Figure 2. Note that cleavage originates from an internal source. (x 50)

As a second illustration, there is the marked effect of a notch on the ductile-to-brittle transition temperature of ionic single crystals. As mentioned earlier highly polished single crystals of silver chloride when tested under impact bending undergo a transition from ductile to brittle behavior when the temperature is lowered below -150°C. If now a V-notch is machined into the crystal the transition temperature is raised to approximately 70°C, i.e., an increase from 0.2 Tm to 0.45 Tm on the homologous temperature scale as shown in Figure 4. [17]

In sodium chloride crystals tested under impact the notch effect can be even more spectacular. While highly polished crystals show a transition at approximately 0.6 Tm (Figure 1) crystals containing a small cleavage notch continue to fracture by cleavage up to within 10°C of the melting point (0.99 Tm) [19] Figure 5 illustrates the fracture surface appearance of a sodium chloride crystal cleaved in this manner at 750°C (0.96 Tm).

Since magnesium oxide may be classified with sodium chloride from the point of view of its cleavage tendency under impact, (Figure 1), it is anticipated that single crystals of this material will, under similar loading conditions, cleave in the presence of a sharp notch at temperatures in excess of 2500°C.
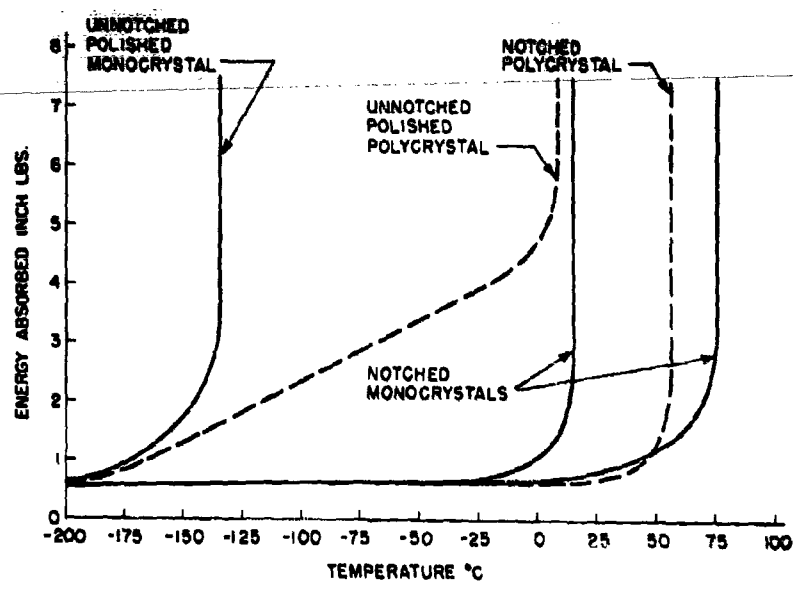
Figure 4 - Ductile-brittle transition curves for silver chloride mon-
crystals and polycrystals in the notched and unnotched
condition impacted at a deflection rate of 110 inches sec^{-1}.
The unnotched monocrystal had cubic orientation. The
notched monocrystals had cubic orientation (transition tempera-
ture 70°C) and an orientation less favorable for cleavage
(transition temperature 10°C).

Figure 5 - Fracture surface of a notched sodium chloride crystal im-
pacted in bending at 750°C (0.96 Tm). Deflection rate
110 inches sec^{-1}. (x 50)

CRACK NUCLEATION MECHANISMS IN IONIC SOLIDS

Since the mechanical behavior of an ionic solid is so sensitive to the presence of a notch, it is important to enquire of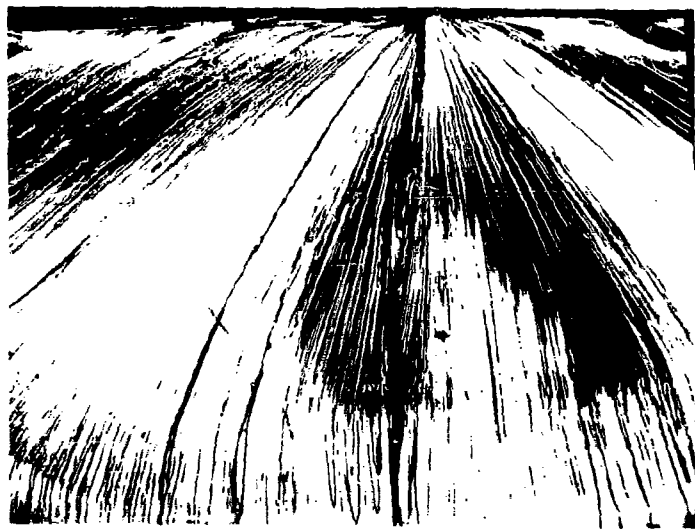 the various ways in which notches may be formed. We will exclude from this discussion cracks introduced by mechanical contact even though it is an intriguing characteristic of these solids that, with the exception of silver chloride, they can be damaged so easily by very light impact at room temperature.[18] Rather we will be concerned with the development of cracks as a consequence of plastic flow or the application of stress to a specimen. A number of independent mechanisms have now been identified; these will be presented in turn.

Crack Nucleation at Surface Precipitates

It has recently been demonstrated that cracks can be nucleated at deposits formed as a consequence of surface reaction.[18] [20] [21] For example, when sodium chloride is removed from water and dried in air, the thin layer of water adhering to the crystal becomes supersaturated and redeposits sodium chloride on to the crystal surface. Attempts to bend such crystals result in the formation of cracks at the interface between the crystal and the deposits as shown in Figure 6. The observation that such deposits are effective in forming cracks only when they lie on surfaces through which edge dislocations emerge suggests that the latter pile-up at the interface between the substrate and the surface deposit.*

It has also been suggested that the stress concentration associated with surface steps produced by dissolution and redeposition can nucleate the cracks.[20] More general aspects of surface and other environmental effects have been reviewed by Machlin elsewhere.[22]

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*   With careful techniques, it is possible to avoid surface deposits altogether, in which case sodium chloride crystals are quite ductile (Figure 2) and remain so indefinitely.[18] The Joffé effect arises from the removal of surface notches by dissolution as originally suggested by Joffé himself.[13]
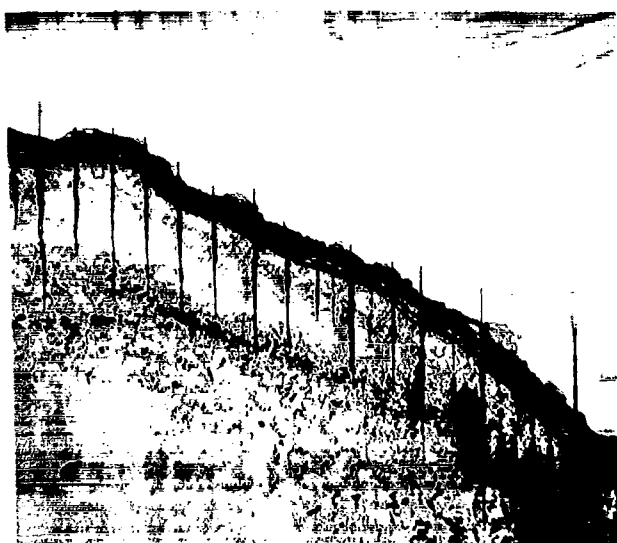
Figure 6 - Formation of cracks at a surface deposit on sodium chloride. Cracks form all along rim of the deposit where it is thickest. (x 50)

Crack Nucleation Due to Slip Band Interaction

Cracks can be generated by plastic flow in ionic crystals not only at an inter-
face but also by the interaction of dislocations moving on intersecting slip
planes. A number of examples of this phenomenon have been reported in
magnesium oxide and in irradiated lithium fluoride deformed at low strain
rates at room temperature. In the latter case cracks lying in (100) planes
have been found to nucleate at the intersection of a pair of conjugate (110) slip
planes; a similar situation has been observed on magnesium oxide. [23] [24]
A study of the crack and slip configurations in the region of pyramidal inden-
tations has led Keh, et al, to propose that cracks can nucleate by the piling
up of dislocations on two (110) slip planes making an angle of 120° to each
other. [25]

It has also been shown in studies on magnesium oxide crystals loaded in
tension, compression, and bending that a crack lying in a (110) plane can
be nucleated at some point along a [100] line (AB in Figure 7) of intersection
of two (110) slip bands. [26][27][28][29][30][31] The crack propagates, under
the influence of the local stress concentration, over the (110) plane until it
meets another (110) slip band in its path where it is arrested. The crack can
then only spread along the channel between the two slip bands to form a stabi-
lized narrow (110) [100] slit, ABCD in Figure 7. Eventually the slit switches
out of the (110) plane into the (100) plane CDEF and propagates to fracture
the specimen. Figure 8 shows the relation of a number of such slits to the
distribution of slip bands in a crystal which has been deformed by bending.

One of the consequences of this mechanism is that the fracture behavior and
thus the ductility of magnesium oxide is critically dependent on the distribution
of slip. For example, when a crystal is loaded in uniaxial tension and the
number and distribution of dislocation sources are such that slip is confined
to one set of slip planes throughout large regions of the crystal, complete

NUCLEATION   STABILIZATION   WIDER SLIP BAND
SLIP BAND   SLIP BAND   (110) PLANE)
($\bar{1}$10) PLANE   ($\bar{1}$10) PLANE)

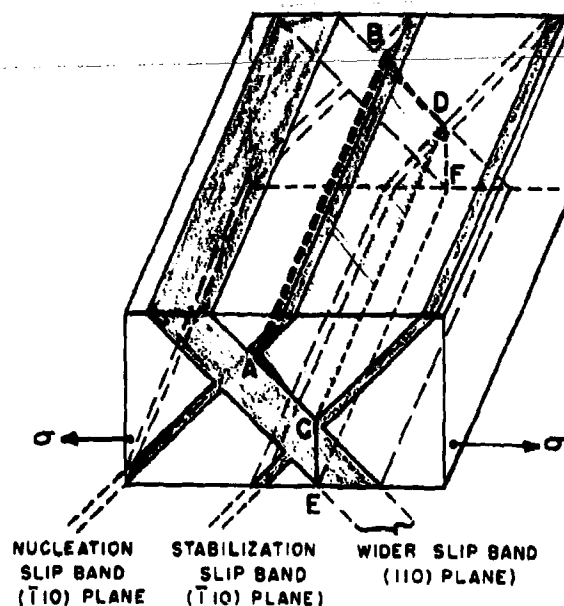Figure 7 - Formation of cracks at slip band intersections. Crack
nucleates along AB, propagates by cleavage over (110)
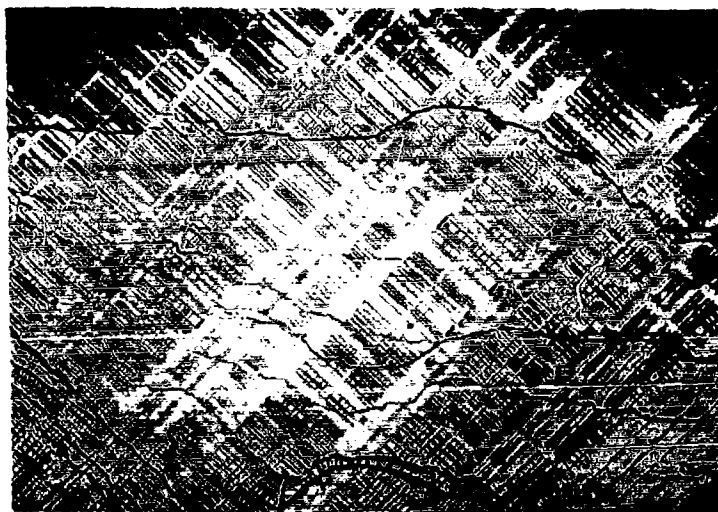and is then stabilized along CD to form a slit ABCD.

Figure 8 - Formation of cracks at slip band intersections in magnesium
oxide. The slip bands are revealed by etching. Note the
cracks lie at the edge of the slip bands and their length is
equal to the spacing between slip bands. (x 150)

intersection of slip bands is avoided and a necessary condition for crack nucleation eliminated. Such a crystal may exhibit as much as 7% plastic strain in tension before fracture. [26] The crack stabilizing effect of neighboring slip bands further increases the critical nature of slip band distribution. Should two orthogonal bands intersect one another to nucleate a crack at the onset of plastic flow complete fracture may occur immediately, either because a stabilizing slip band is not available to limit the size of the crack or if it is available it is too far away from the nucleating site to stop it. When plastic flow occurs by slip on very closely spaced bands in two conjugate systems (this distribution of slip may be accomplished by introducing dislocation sources artifically on all surfaces of a crystal to be deformed in bending) the ductility is again quite high and when fracture occurs it no longer originates from a simple (110) [100] internal slit. [26] Indeed slit formation is completely suppressed within the resolution of the optical microscope. Instead cleavage fracture originates from another type of source which will now be briefly described.

When an elastic beam undergoes severe bending the tension surface becomes curved due to Poissons contraction. A crystalline solid can accommodate this anti-clastic curvature by developing kinks near the specimen corners, (Figure 9). While the details of "anti-clastic kinking" have yet to be properly worked out, the ease with which it may be accomplished appears to depend in some way upon the fundamental plasticity of the solid at the particular test temperature. For magnesium oxide anti-clastic kinking is a difficult process at room temperature (although it has been occasionally observed) and the crystal cannot easily relax the lateral stress across the beam other than by cracking. Consequently, when a crack is nucleated it propagates along the length of the beam before switching to the plane normal to the applied stress, thus leaving a very complex fracture surface. [26] Examples of longitudinal cracks in a magnesium oxide crystal for which the slip is both dense and uniform are included in Figure 10.

TENSION SURFACE

NEUTRAL AXIS

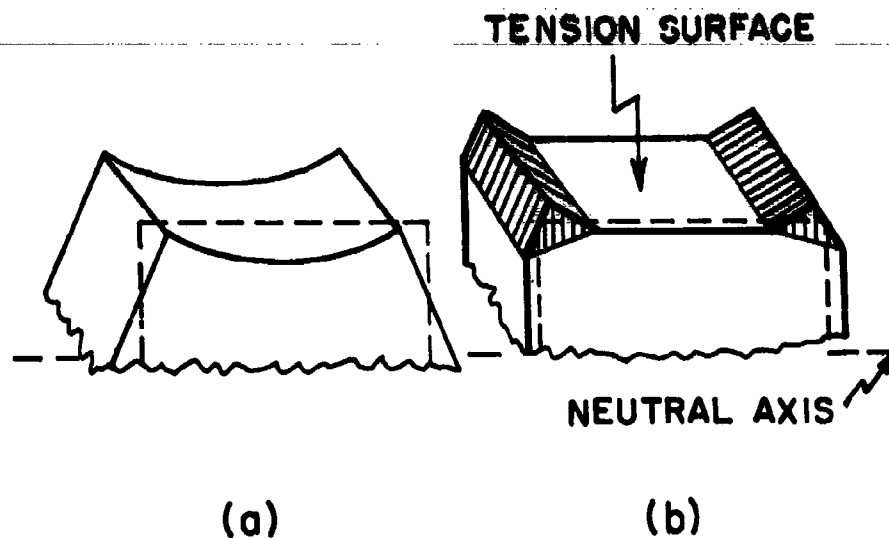**(a)**   **(b)**

Figure 9 - Change in cross-sectional shape of a bent beam. (a) Anti-
clastic curvature of an elastic solid (b) Anti-clastic kinking
of a crystalline solid.

Figure 10 - Formation of complex longitudinal cracks in the tension
surface of a magnesium oxide crystal. Tensile axis
vertical. Crystal was sprinkled with silicon carbide be-
fore loading to produce dense slip. (x 50)

In lithium fluoride and sodium chloride crystals it is possible to obtain similar
types of fracture behavior in bending by altering the temperature of loading.
For example, lithium fluoride crystals when bent at room temperature at a
low strain rate (10^{-5} sec^{-1}) behave rather like magnesium oxide crystals when
slip is finely spaced. At liquid nitrogen temperature, the distribution of slip
is such that lithium fluoride crystals fracture after the formation of stable
slits in the manner exhibited by polished magnesium oxide at room temperature.
Sodium chloride crystals loaded in bending at a fairly high surface strain rate
(10^{-1} sec^{-1}) at liquid nitrogen temperature often fracture from a primary ori-
gin near one of the anti-clastic kinks which can still form in these crystals at
this temperature. A crack spreads from this origin between slip bands to
form a (110) slit which then serves as an origin for (100) cleavage. These
examples suggest that there must be many possible sequences of fracture in
single crystals of these materials. The particular sequence and source chosen
depends in a way yet to be clarified upon the distribution of slip, temperature,
strain rate and type of loading.

The role of temperature can be important in three ways. The first is based
on the assumption that dislocation sources are unlocked with the aid of thermal
energy so that at higher temperatures a greater number of dislocation sources
are activated and the slip band spacing is correspondingly smaller. Second,
temperature is one of the factors known to determine the dislocation density
within a slip band. [10] Slip bands formed at low temperatures where the den-
sity is greatest are more effective barriers and dislocations moving on ortho-
gonal planes are likely to form cracks more readily. Third, an increase in
temperature enhances cross slip thereby relieving the local stress concentra-
tions which arise at slip band intersections. It is interesting to note that the
dislocation density in slip bands in magnesium oxide at room temperature is
similar to that in lithium fluoride at liquid nitrogen temperature and irradiated
lithium fluoride at room temperature. All three are associated with the forma-
tion of cracks at slip band intersections.

Crack Nucleation in Polycrystalline Material

It would appear reasonable to assume that the crack nucleation mechanisms described for the monocrystals above should also occur in polycrystals under appropriate conditions. However, experience has shown that in general inter-granular separation is the dominant feature of crack initiation in polycrystalline material. We will find it convenient here to distinguish between the low and high temperature behavior.

Low Temperature Intergranular Fracture   -   Recent studies by Westwood on bi-crystals of magnesium oxide loaded in compression at room temperature, have shown that cracks can form at a given grain boundary through the interaction of edge dislocations on both sides of the boundary. [32]   Significantly these cracks do not generally lie along the grain boundary itself but are formed in the cleavage planes of the individual grains as shown in Figure 11. It is important to bear in mind, however, that these experiments were performed on bi-crystals for which the grain boundaries were fairly simple in nature and for which the misorientation was of the order 10 - 20°. In polycrystalline material containing a large number of equiaxed randomly oriented grains the fracture origin is invariably intergranular. We have found that at low homologous temperatures polycrystalline rods of sodium chloride, lithium fluoride and silver chloride always fracture by cleavage from a primary origin located at the periphery of an intergranular surface.   A typical example is shown in Figure 12. Frequently it is possible to detect a number of other ruptured grain boundaries within the transparent rods (Figure 13), but generally the very first intergranular crack which forms gives rise immediately to catastrophic cleavage failure.

These polycrystalline rods have been prepared by the recrystallation of high purity single crystals during extrusion and are, therefore, free from large pores and excessive grain boundary impurity segregation. Furthermore, the fact that

Figure 11 - Formation of cleavage cracks at grain boundaries in compressed
bi-crystals of magnesium oxide. Grain boundary runs from upper
left to lower right. Slip bands revealed by etching. (x 125)
(After Westwood [32]).

Figure 12 - Intergranular source of cleavage fracture in polycrystalline sodium chloride. (x 200)
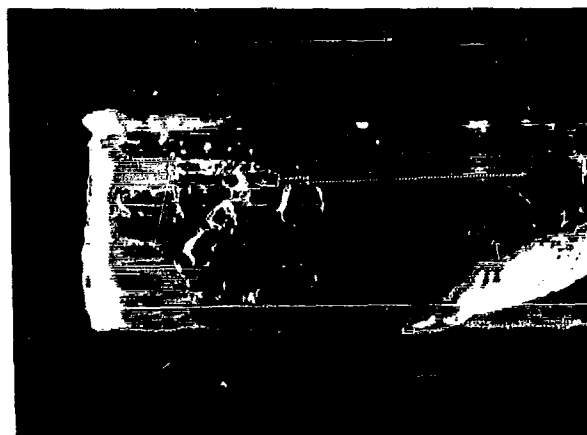

Figure 13 - Formation of intergranular cracks in polycrystalline sodium chloride. The rod has fractured at the left but other grain boundaries have ruptured under the bending load. (x 7)

the intergranular source can be completely internal as in Figure 12 indicates that environmental embrittlement is not the factor responsible for grain boundary failure under stress.

Macroscopically the sodium chloride and lithium fluoride specimens appear completely brittle even when loaded carefully at a low strain rate (10^{-5} sec^{-1}). The stress strain curves rise elastically up to the fracture stress which for sodium chloride varies between 1,000 and 4,000 psi, always well in excess of the yield stress of single crystals (approximately 400 psi). However, under the polarising microscope the stress birefringence pattern clearly shows that a limited amount of slip has taken place before fracture.

To interpret these observations it is proposed that grain boundaries in ionic solids have low cohesive strengths which could well originate from electro-static faulting which must be present in a boundary between two randomly oriented grains. The strength of a given grain boundary is determined by the relative misorientation across it and will be greatest for fairly simple small angle boundaries or boundaries for which the electrostatic misfit is low. Grain boundaries rupture when the local stress arising from the plastic constraints imposed upon one grain by its neighbors exceeds the cohesive strength. Such constraint stresses may be identified with the interactions between dislocations held up at the boundaries.

Reasons for the difference in crack location in the bi-crystals and the more typical polycrystalline materials described here are two-fold.[32] In poly-crystalline materials there are triple lines running through the solid along which three grains meet and points where as many as six grains may be in juxtaposition. At these points the local constraint stresses are particularly high. On the other hand the two grains of a bi-crystal specimen are not sub-jected to such high multiaxial constraint stresses. Second, it must be remem-bered that the polycrystal rods were pulled in tension whereas the bi-crystals

were loaded in compression. In the former case, it was always probable that a boundary of low cohesive strength existed across which the resolved tensile stress was quite high. In the bi-crystals there was a compressive stress across the boundary so that growth of a crack along the boundary was discouraged, instead it preferred to grow in cleavage planes more nearly parallel to the compression axis.

Studies on silver chloride deformed in uniaxial tension at a low strain rate over a range of temperature have demonstrated the importance of the slip mode in relieving grain boundary constraints by plastic flow.[33] At room temperature and -78 °C the individual grains deform by wavy glide and can easily conform to the grain boundary distortion, at these temperatures polycrystalline silver chloride is quite ductile (at low strain rates) and the cross section reduces to a point. At -196 °C the grains deform by straight slip and the plastic constrains are not so easily accommodated, silver chloride then fractures brittlely from an intergranular source after a slight amount of plastic deformation but with no reduction in cross sectional area at fracture.

The work on silver chloride has been extended by studying the effect of temperature on the fracture behavior at higher strain rates (100 sec^{-1}). The energy absorbed under impact for carefully polished bars of polycrystalline silver chloride in both the unnotched and notched condition is plotted in Figure 4. The curves do not extend beyond the transition temperature range because such specimens merely bend without fracture. It is important to note three things: first, that the ductile-brittle transition temperature for unnotched polycrystalline material occurs at a higher value than for single crystals. Second, the energy absorbed by unnotched specimens rises fairly gradually up to the temperature at which they do not fracture at all, this temperature being only slightly less than for notched single crystals. Third, the ductile-brittle transition temperature for a notched polycrystalline specimen lies within the range characteristic of notched single crystals. The interpretation of this

behavior is that under impact bending, polished polycrystalline material develops notches by grain boundary separation which then nucleate cleavage. As the temperature is raised an increasing amount of plastic deformation precedes the grain boundary failure and more energy is absorbed during the test. Confirmation of the occurrence of plastic flow before rupture can be obtained by examining the primary intergranular origin on both halves of the fractured specimen. As can be seen in Figure 14, for specimens impacted at temperatures midway in the transition zone (-90°C) and higher, slip traces can be found in mirror image configurations indicating that slip must have been punched across the grain boundary before it separated. At lower temperatures the intergranular origin surfaces are free from evidence of slip. When a machined notch pre-exists before impact there is much less expenditure of energy by plastic flow until the notch transition temperature is exceeded.

Normally, sodium chloride, lithium fluoride, and magnesium oxide deform by planar slip on six systems at room temperature. These systems evidently do not provide adequate flexibility to relieve boundary constraints and consequently macroscopic ductility is not measured at this temperature. At higher temperatures where sodium chloride and lithium fluoride monocrystals deform by wavy slip, the polycrystalline forms become ductile at moderate strain rates (10^{-1} sec^{-1}) but nevertheless, grain boundary cracks still form. At high strain rates (100 sec^{-1}) polycrystalline sodium chloride and lithium fluoride remain completely brittle at all temperatures. On the basis of the behavior of silver chloride in Figure 4, it may be anticipated that polished specimens of polycrystalline sodium chloride and lithium fluoride should begin to absorb energy above 0.6 Tm (transition temperature of the single crystal, Figure 1), the fact that they do not is a consequence of their high temperature fracture behavior which will now be discussed.

Figure 14 - Slip markings in matching intergranular surfaces. These surfaces are the primary fracture origin for a polycrystalline silver chloride specimen impacted at -48°C. Note the mirror image configuration of the slip markings. (x 150)

High Temperature Intergranular Fracture   -   Recent work by Adams and
Murray has shown that bi-crystals of sodium chloride and magnesia can under-
go extensive grain boundary shear at an astonishingly high rate when the tem-
perature exceeds 0.5 Tm. [34]   They conclude that the rate of shear is sensi-
tive to the applied stress, temperature and misorientation of the boundary. It
is found that simple low angle boundaries ($\lesssim 5°$) have a high shear resistance
whereas complex boundaries have a low shear resistance.

Grain boundary shear becomes a more severe problem when the boundary has
a jog in it, for the displacement then results in the formation of a void within
the material as shown in Figure 15. This observation is particularly signifi-
cant for in a more typical polycrystalline material displacement over any inter-
granular surface must necessarily lead to the development of a wedge shaped
void along the triple lines and other regions where a number of grains are in
juxtaposition. The failure of polycrystalline lithium fluoride at 400°C due to
intergranular sliding is reproduced in Figure 16. This mode of failure does
not necessarily involve dislocation interaction at the boundary to provide a
stress concentration so there is little energy absorbed by plastic flow. Further-
more, once a crack has started in this way it is able to propagate intergranu-
larly with no further absorption of energy, the material merely slides apart to
give complete intergranular rupture. This can occur even at high strain rates.

In summary, there are two mechanisms by which pure polycrystalline material
is embrittled, one at high temperatures, the other at low temperatures. The
extent to which they overlap depends on the strain rate. The temperature at
which intergranular shear failure becomes important (namely 0.5 Tm) appears
to be relatively unaffected by the applied strain rate. On the other hand inter-
granular fracture at low temperatures arises from dislocation interactions at
grain boundaries; under these conditions the higher the applied strain rate then
the higher the temperature must be for unnotched polycrystals to manifest
ductility before fracture. When carefully prepared rods of sodium chloride are

Figure 15 -   High temperature (600°C) intergranular shear in a bi-crystal
of sodium chloride. This boundary has a jog in it which forms
a void upon displacement. (x 100). (After Adams and Murray[34]).

Figure 16 -   Intergranular cracking produced by grain boundary sliding in
the tension surface of a lithium fluoride polycrystalline rod.
Loaded in simple bending at 400°C at a nominal maximum
strain rate of 10^{-1} sec^{-1}. (x 100)

loaded at a high strain rate, the temperature at which intergranular fracture due to dislocation pile-up disappears is so high that intergranular shear failure takes over and the material is completely brittle at all temperatures. For silver chloride under similar loading conditions there is sufficient plasticity at a temperature low enough to avoid fracture by grain boundary shear and the ductile-brittle transition is observed. Only when a low strain rate is employed can a similar transition be produced in sodium chloride, lithium fluoride, or magnesium oxide.

FACTORS CONTROLLING CRACK PROPAGATION

In the preceding sections we have discussed qualitatively the formation of cracks in single crystals and polycrystalline ionic solids without reference to the quantitative aspects involved. This is because there is an unfortunate paucity of experimental evidence regarding the effects of grain size, temperature, strain rate, and thermal-mechanical history on the fracture stress of fully dense ionic materials. In spite of the absence of such information there is no 'a priori' reason why it could not be assumed that cracks are formed (or pre-existing cracks accelerate from rest) when a critical stress is exceeded which complies with a Griffith-type energy balance relationship. For crack nucleation the energy balance equation must embody a term describing the particular dislocation interaction responsible for crack formation in the manner adopted by Stroh, Petch and Cottrell for metals. [35][36][37] The marked effects of strain rate and temperature upon the degree of deformation prior to crack nucleation is undoubtedly a consequence of the way in which these parameters influence the conversion of dislocations into cracks at slip band intersections or grain boundaries. However, even if we could relate in detail the parameters which must be taken into account for crack nucleation it would not necessarily help in a discussion of notch sensitivity, with which we are primarily concerned here. For notch sensitivity it is more significant to consider a second form of the energy balance equation which allows for the velocity of a moving crack.

Mott, Gilman and Stroh have shown how crack velocity depends not only on the elastic energy release and the surface energy of the solid but also on (a) the kinetic energy associated with the rapid sideways displacement of material on either side of the crack and (b) the plastic deformation which may accompany crack propagation. [38][39][40] In a crystalline solid the velocity of a cleavage crack may be written: [39]

$$v = KV_0 \left[1 - \frac{U_w}{U_e} \right]^{1/2}$$

where K is a constant found experimentally to be of the order 0. 3, V_0 is the velocity of sound, U_e is the elastic energy released, and U_w is the energy dissipated during crack growth. The ratio U_w/U_e determines whether V has a finite value or not. If U_w is less than U_e the velocity quickly increases to the terminal value KV_0. If U_w is greater than U_e, crack growth is energetically impossible.

It is important to consider the parameters influencing the ratio U_w/U_e. U_e is the driving force for crack growth and is proportional to $\sigma^2 L^2 /E$ where σ is the applied tensile stress, L is the crack length and E Young's Modulus. The energy dissipated during crack growth, U_w, may be represented as the sum of two terms, U_s and U_d. U_s is the surface energy of the crack faces and is equal to $2A\Upsilon L$, where Υ is the specific surface energy of the solid and A is a numerical factor slightly greater than unity which takes into account the extra surface area due to fracture surface steps and other irregularities. U_d is a term which accounts for the energy dissipated by plastic flow at the tip of a crack and at tear lines.

Earlier it was pointed out that slip bands can arrest or modify the early growth of cleavage cracks in magnesium oxide, lithium fluoride, and sodium chloride. This stabilization arises from an increase in U_s through an increase in the factor A since in cutting through the screw dislocations of a slip band a large number of cleavage steps are formed. It is much less effective, however, when larger cracks are formed and move at higher stress levels. For example, when a polished sodium chloride crystal undergoes 50% plastic strain in uniaxial tension it still fractures by catastrophic cleavage from an internal

source (Figure 3). Although such a crystal may be regarded as ductile in that it deforms substantially before fracture, it is still notch sensitive.

U_d can attain values several orders of magnitude greater than U_s and for this reason is the most important factor to be considered here. U_d can be written as Bv^{-n} where v is the crack velocity and B is a term describing the plasticity of the solid. U_d is an inverse function of v because the latter determines the time for which material at or ahead of the crack tip is subjected to the applied stress. [40] The factor B increases rapidly with temperature and with the shear stress just ahead of the crack (or within the threads of material at tear lines). In addition B is proportional to the volume of plastically deformed material. It follows then that the value of U_d and thus the ratio U_w/U_e will decrease rapidly with an increase in crack length and crack velocity, a decrease in temperature and with a greater degree of triaxiality of stress ahead of the crack.

Single Crystal Behavior

Experimental evidence presently available suggests that ionic solids, in common with other semi-brittle solids, become notch insensitive only when the temperature and rate of loading are such that substantial plastic flow can occur at the tip of the notch. In this respect the most interesting observations have been made on notched silver chloride monocrystals, where there is a significant change in the cleavage fracture appearance as they are impacted at temperatures within the transition range (Figure 4). Below -15°C such crystals fracture entirely by high velocity cleavage as in Figure 17 (a). Above this temperature a cleavage crack nucleated near the root of the notch cannot attain the critical velocity without first growing discontinuously at a relatively low average velocity accompanied by considerable plastic flow. The macroscopic appearance of a crystal impacted at room temperature is shown in Figure 17 (b). The extent to which the crack grows discontinuously and the
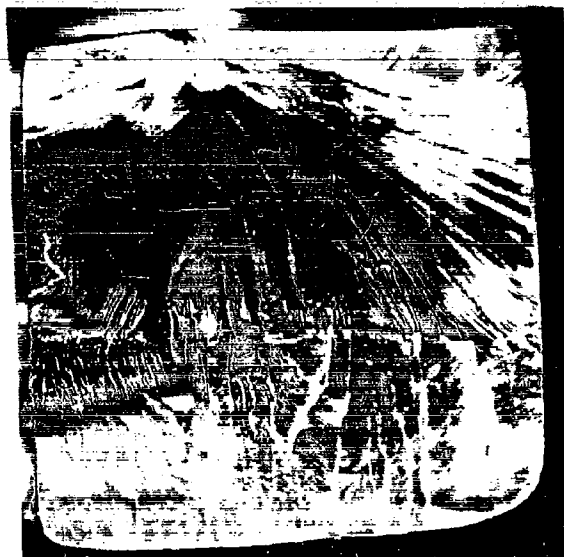
Figure 17(a) - Cleavage fracture surface of a silver chloride mono-crystal
impacted below its transition temperature. (x 10)

Figure 17(b) - Fracture surface of a notched silver chloride mono-crystal
impacted within transition range (25°C). Note the "thumb-
nail" region immediately below notch where cleavage crack
propagated discontinuously. Discontinuous cleavage was
manifested again on side opposite notch just before final
separation. (x 10)

associated plastic flow both increase markedly with temperature through the transition range. Above 75°C the crack can still be nucleated but never attains the catastrophic velocity, instead the specimen bends into a U-shape without complete fracture. Above 80°C the machined notch merely widens without the generation of any cleavage cracks. This change in behavior in silver chloride is a particularly striking example of how an increase in plasticity with a small increase in temperature can alter the character of crack propagation from one in which a crack can achieve catastrophic high velocity over very short distances to one in which cracks do not propagate at all.

The fracture surface markings accompanying the slow discontinuous crack growth are quite characteristic. Steps are left in the surface which define the successive positions of the crack front where the latter either stopped or slowed down sufficiently for plastic flow to blunt the tip. Figure 18 is an optical micrograph of the fracture surface of a crystal impacted at 0°C in the region where catastrophic cleavage has supplanted the propagation by discontinuous cleavage. The tear lines produced during this low velocity cleavage mode are irregular, discontinuous and show evidence of extensive local plastic deformation. The contrast in the appearance of tear lines produced during high and low velocity cleavage may be compared directly in the electron micrograph of Figure 19.

The discontinuous nature is thought to arise in the following way. A crack propagating at a temperature and velocity which allows plastic deformation experiences a retardation due to the increase in U_d, this lowers the crack velocity causing U_d to increase still further. The effect of plastic flow is autocatalytic and the crack very quickly comes to rest with a blunted tip. At a constant load in a stiff system the crack would of course, remain at rest, but when the two halves of the crystal are pulled or driven apart rapidly (as in the impact test) the stress applied to the crack must increase rapidly enough to cause the latter to jump forward when a Griffith-type energy balance

Figure 18 - Transition from discontinuous (low average velocity)
cleavage to catastrophic (high velocity) cleavage in a
notched silver chloride monocrystal impacted at 0°C.
Propagation direction, top to bottom. Note the well de-
fined striae in discontinuous region which indicate suc-
cessive positions of the crack front. (x 330)

Figure 19 - Electron micrograph of transition from discontinuous to
catastrophic cleavage. The tear lines in the discontinuous
region (upper part of the figure) show evidence of extensive
local plastic flow. (x 2000)

is satisfied and so repeat the propagation cycle. The fracture surface mark-
ings suggest that each time the crack moves, it does so by accelerating from
rest rather than by the advanced nucleation of a new crack.

In silver chloride the peripheral steps which remain in the fracture surface
are spaced at remarkably regular intervals right up to the time when a por-
tion of the crack front attains the critical velocity for catastrophic growth.
The step spacing from the root of the notch appears to be characteristic of
the imposed loading rate and temperature, e. g. , in the case of silver chloride
impacted at room temperature, this is of the order 2-3 μ, other evidence at
liquid nitrogen temperature and a lower strain rate indicates the correspond-
ing spacing is about 25 μ.

Gilman has demonstrated a closely related effect in lithium fluoride by passing
cleavage cracks through a monocrystal at different speeds at room tempera-
ture. [41] At terminal speeds ($K V_o = 2 \times 10^5$ cm/sec) cracks pass through
the crystal without nucleating dislocations. It is not until the crack velocity
drops to a critical value of 6×10^3 cm/sec that dislocations are generated
along tear lines. At a slightly lower speed of 3×10^3 cm/sec propagation
becomes discontinuous and wherever the crack stops or slows down temporar-
ily dislocations are generated along the crack front. While the number of dis-
locations involved is insufficient to produce slip lines, etching techniques can
be used to reveal their presence (see Figure 20). Similarly, discontinuous
propagation during the acceleration of cleavage cracks from rest in magnesium
oxide has been observed by Clarke and Sambell. [27]

It is evident from the observations on silver chloride that the disappearance
of notch sensitivity in single crystals coincides with the appearance of dis-
continuous cleavage which is concomitant with the condition that substantial plas-
tic flow can occur at a moving crack tip at a rate sufficient to maintain U_w greater

than U_e.   The ductile-to-brittle transition of prenotched material, therefore, depends fundamentally on the innate plasticity of the solid. In sodium chloride, and presumably lithium fluoride and magnesium oxide, the condition that plastic flow can occur rapidly enough to eliminate notch sensitivity at the deflection rate considered above (110 inches per sec) is not met even at a homologous temperature of 0.95 Tm (750°C, see Figure 5). However, when the deflection rate at the notch is reduced to a quarter of the above value discontinuous low velocity cleavage (analagous to that observed in silver chloride) appears at the root of the pre-existing cleavage notch above temperatures of 0.85 Tm as shown in Figure 21. It appears reasonable that at lower deflection rates still, the temperature at which cleavage becomes unstable will be correspondingly lower and that a brittle-to-ductile transition will be observed in notched single crystals.

The reason why sodium chloride can undergo catastrophic cleavage at much higher homologous temperatures than silver chloride is an important point which is not entirely understood. It is not simply a matter of the relative mobility and multiplication of dislocations, per se, for both crystals are equally soft at room temperature (the critical resolved shear stress is about 200 psi in each case) and both can undergo extensive deformation at a low strain rate. The contrast between the two solids must be a reflection of fundamental differences in the nature of their ionic bonding. Mott and Gurney have pointed out the relatively greater importance of Van der Waals bonding in salts of the silver halide type compared with that in the alkali halides. [42] This is due to the greater polarizability of silver ions. Such differences in ionic character can affect the dislocation core structure and dislocation mobility over the respective potential slip planes of the crystal, namely (100), (110), and (111). [43][44] The greater the number of slip systems which can be brought into rapid operation, the more degrees of freedom the solid has to relax the stresses at a moving crack tip. At present we know that silver chloride deforms at low strain rates by pencil glide on all three potential slip
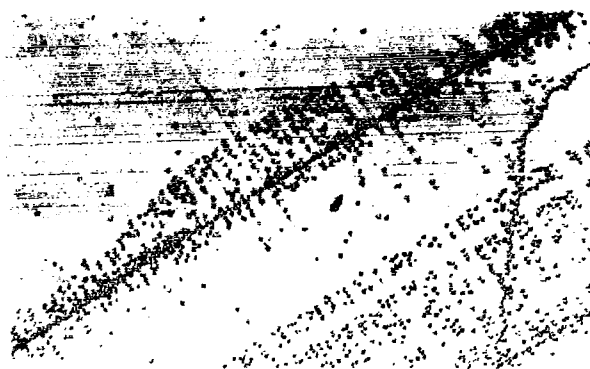
Figure 20 - Dislocations nucleated along the periphery of an arrested crack in lithium fluoride. (x 250) (After Gilman et al.[41]).

Figure 21 - Fracture surface of a notched sodium chloride crystal impacted in bending with a deflection rate of 27 inches sec^{-1} at 650°C. Fracture starts at top by discontinuous cleavage which later switches to catastrophic cleavage. Note thermal erosion of cleavage lines. (x 250)

planes which share a common (110) slip direction, at temperatures above -196°C. Sodium chloride does not do so until at least 300 - 400°C is reached.

In a similar connection Gilman has pointed out that, in the rock salt structure, shear on (110) planes whose zone axis is parallel with the crack front brings the ions across the face of the crack into repulsive position.[45] The additional electrostatic energy provides a resistance to dislocations moving from the crack tip. Again it is to be expected that electrostatic faulting would provide a lower resistance for dislocation motion in silver chloride than for the other three rock salt structure materials.

Polycrystalline Behavior

It is important to consider what effects grain boundaries may have on crack propagation and, thereby, on the fundamental notch sensitivity of ionic solids. Again, because of the convenience of preparation and the temperature range in which it may be studied experiments have been conducted on the behavior of notched polycrystalline silver chloride (prepared by the extrusion of mono-crystals). Comparing the fracture surfaces of a series of specimens frac-tured under impact over the transition temperature range we find exactly the same change in appearance as for monocrystals. Moreover, the temperatures at which the different modes of cleavage are manifest are essentially the same; this substantiates the conclusion which may be drawn from the energy absorp-tion curves of Figure 4 that the presence of grain boundaries has little or no effect on the ductile-brittle transition temperature of notched silver chloride.

Below the transition range, catastrophic cleavage propagates from a primary origin near the notch and there is no evidence that grain boundaries afford any special resistance to crack growth. The marginal increase in U_s which re-sults from an increase in the height and density of the tear lines as the high velocity crack sweeps across the boundary is not sufficient to arrest its growth.

In the transition range, cracking first occurs by the growth of low velocity discontinuous cleavage cracks in one or in several grains along the root of the notch. At the lower temperature end of the transition range the discontinuous cleavage switches to catastrophic cleavage before the former has even reached the first grain boundary as shown in Figure 22. As the temperature increases within the transition range and the discontinuous cleavage extends deeper there is evidence that grain boundaries can serve as effective barriers. There are many examples of stable microcracks which have fractured by discontinuous cleavage up to the grain boundary and stopped, later to be isolated by the catastrophic cleavage as it sweeps past (see right hand side of Figure 22). This observation does suggest that an extremely fine grain size, where the grain dimension approximates the spacing between successive positions of the crack front (i.e., 2 - 3 μ),might have some effect on the notch sensitivity. However, it is anticipated that this will only be a second order effect and that grain size refinement will not lower the transition temperature markedly. The grain sizes studied here (30 μ to 200 μ) are so large that the conditions at a moving crack tip are essentially the same as for a monocrystal, and cannot be expected to alleviate notch sensitivity at all.

On the basis of the behavior of silver chloride polycrystals we should expect to find that sodium chloride polycrystals become notch insensitive under comparable loading conditions only at temperatures well above 0.85 Tm, where discontinuous cracking is observed in the monocrystal (Figure 20). Unfortunately, it is not possible to confirm this effect because, as mentioned earlier, at temperatures greater than 0.5 Tm the fracture changes to one of complete intergranular separation. Moreover, it is not anticipated that re- fining the grain size will lower the transition temperature sufficiently for notch insensitivity to be manifest below the melting point. Only by lowering the strain rate considerably will it be possible to avoid the complications of grain boundary shear and fracture. Similar conclusions apply to the behavior of notched polycrystalline lithium fluoride and magnesium oxide tested under impact.
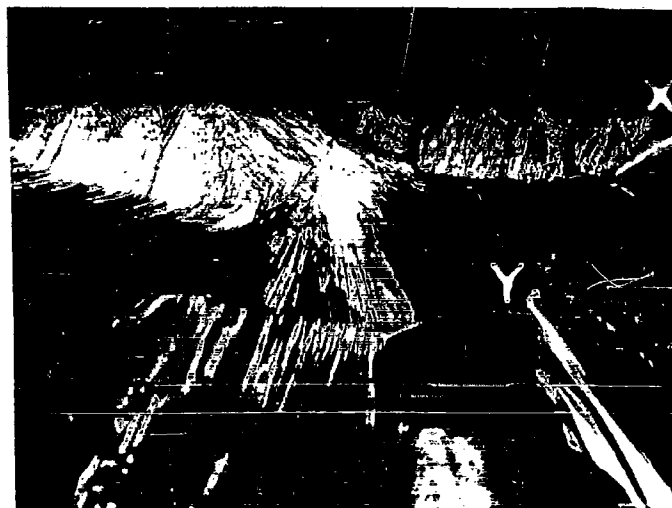
Figure 22 - Fracture surface of a notched polycrystalline silver chloride specimen impacted within the transition range (55°C). Note the series of points along the root of the notch from which cleavage propagated discontinuously. The grain boundary XY has restricted discontinuous propagation at the far right of the specimen. (x 100)

Effect of Stress State

Whenever a brittle crack approaches a free surface, the hydrostatic component of the applied stress diminishes and the ratio of maximum shear stress to maximum tension stress (and therefore U_w/U_e) increases with the result that the probability of plastic flow occuring in the region of the crack tip also increases. The consequences of this are manifest in a number of ways. First, it may be seen in the fracture surface of notched single crystals impacted in the transition range. As the high velocity cleavage crack approaches the free surface opposite the notch there is an increasing tendency for it to stall and revert to the discontinuous crack propagation by which it started from the notch. This may be seen in Figure 17 (b) and is illustrated in greater detail in the photomicrograph of Figure 23. It may also be seen in the fracture surface of polycrystalline material impacted in the transition range. A brittle crack advances through polycrystalline material in a most irregular manner, either by transgranular cleavage or intergranular cracking. Sometimes the difference in local crack velocity and direction is such that certain portions of the crack front are outflanked by others with the result that high velocity cleavage cracks can find themselves propagating in directions at right angles or opposite to one another. The resulting change in the state of stress in the threads of material between these different segments of the crack front can bring about a local change in the value of U_d and thus the mode of propagation. Discontinuous cleavage due to this is illustrated in Figure 24, where cleavage crack A had apparently outflanked B causing the latter to propagate discontinuously to produce characteristic markings in the surface.

The most striking effect of local changes in the state of stress is observed in polycrystalline silver chloride containing a fine dispersion of spherical alumina powder (average particle size 7 µ). Notched specimens of this material when fractured under impact absorb more energy than pure polycrystalline silver

Figure 23 -   Transition from catastrophic (high velocity) cleavage back
to discontinuous (low average velocity) cleavage as a brittle
crack approaches a free surface. Notched silver chloride
monocrystal impacted at 65°C. Propagation direction, top
to bottom. Compare with Figure 18. (x 330)

Figure 24 -   Discontinuous propagation of cleavage across thread of
material left between cleavage facets A and B in poly-
crystalline silver chloride. (x 100)

chloride alone and the transition temperature is depressed. [46] A high reso-
lution electron fractographic investigation of the fracture surface shows it to
contain regions of extensive discontinuous cleavage at temperatures below the
range where it would normally appear. It has been suggested that under impact the material in the shear zone below the root of the notch pulls away from
the spheres to leave internal holes in the path of an advancing crack. These
holes provide many internal free surfaces which cause the brittle crack to become unstable through the many local changes in U_d and to change to the discontinuous mode of cleavage propagation. It should be noted, however, that
such changes in the mode of propagation from catastrophic to discontinuous
cleavage (with the corresponding increased absorption of energy) can only be
promoted (either intrinsically or artificially) at temperatures not very far below the fundamental transiton temperature of the notched single crystal material. Again, it is not anticipated that a similar dispersion can have any
effect on the notch transition temperature of, for example, sodium chloride
because of the high temperature intergranular shear failure.

SUMMARY AND CONCLUSIONS

1. The strength of ionic solids has been discussed in terms of their resistance to fracture. Particular emphasis has been given to their extraordinary notch sensitivity.

2. Ionic single crystals can exhibit considerable ductility before fracture providing the strain rate is low enough and the temperature high enough. However, the mere exhibition of ductility can be misleading for such crystals may remain brittle in the presence of a notch. Notches can be formed in a variety of ways; by mechanical contact, by the interaction of slip dislocations with coherent surface deposits, with other slip dislocations or with grain boundaries.

3. In view of the notch sensitivity, it is most important to consider those factors which influence the propagation of cleavage. Only when substantial plastic flow occurs at the root of the notch can catastrophic cleavage be prevented. The amount of plastic flow depends upon the fundamental plasticity of the solid, the temperature, and the stress state at the crack tip.

4. Grain boundaries invariably embrittle ionic solids in the temperature range in which a single crystal is notch sensitive. This is due to the inherently low cohesive strength of a grain boundary, which ruptures to form a notch (the size of which depends on the grain size) under the constraint stresses developed by limited plastic deformation. Only when these stresses are relaxed by flexible plastic flow can a polycrystalline material be completely ductile.

5. At temperatures in excess of 0. 5 Tm grain boundaries have extremely low shear strength causing polycrystalline material to fail even at high strain rates.

6. This paper has been primarily concerned with the notch sensitivity of ionic solids because we believe this to be the dominant feature of their mechanical behavior. There is at present a critical need to study those factors which influence the fracture stress of these materials, for example, the nature of grain boundaries, grain size, impurity and alloy additions, microstructure, thermal-mechanical history and fabrication techniques.

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